NASA TECHNICAL NOTE



NASA TN D-6147

MODIFICATION OF HIGH-TEMPERATURE COBALT-TUNGSTEN ALLOYS FOR IMPROVED STABILITY

by Robert L. Dreshfield, John C. Freche, and Gary D. Sandrock Lewis Research Center Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION - WASHINGTON, D. C. - FEBRUARY 1971

LEGH LIBRARY RAPB, NA

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TN D-6147		
4. Title and Subtitle MODIFICATION	OF HIGH-TEMPERATURE	5. Report Date February 1971
COBALT-TUNGSTEN ALLOYS	FOR IMPROVED STABILITY	6. Performing Organization Code
		o. Ferrorming Organization Code
7. Author(s) Robert L. Dreshfield, John C.	Freche, and Gary D. Sandrock	8. Performing Organization Report No. E-5944
9. Performing Organization Name and Address		10. Work Unit No. 129-03
Lewis Research Center		
National Aeronautics and Space	e Administration	11. Contract or Grant No.
Cleveland, Ohio 44135		13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address		Technical Note
National Aeronautics and Space	e Administration	14. Sponsoring Agency Code
Washington, D. C. 20546		14. Sponsoring Agency Code
15. Supplementary Notes		<u> </u>
to 2125° F (1094° to 1163° C) r 2000 hours at 2125° F (1163° c alloy design to achieve micros	the cobalt-tungsten (Co-W) system, range was identified. It has an average was identified. It has an average was identified and the structural stability based on a lineating phase in this alloy system, and strated.	erage stress-rupture life of over m ²) in helium. A method of ar relationship between the
17. Key Words (Suggested by Author(s))	18. Distribution Stater	ment
Superalloys	Unclassified	- unlimited
Cobalt-base alloys		
Engine materials		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 22. Price* \$3.00

MODIFICATION OF HIGH-TEMPERATURE COBALT-TUNGSTEN ALLOYS FOR IMPROVED STABILITY

by Robert L. Dreshfield, John C. Freche, and Gary D. Sandrock

Lewis Research Center

SUMMARY

A previously reported NASA cobalt-tungsten (Co-W) alloy series was further investigated for its potential for stator vane application for advanced turbine engines. A vacuum-melted modification of an alloy (VM-103) with a nominal composition in weight percent of 25 tungsten - 3 chromium - 1 titanium - 1 zirconium - 0.4 carbon, and the balance cobalt had excellent high-temperature strength, over 2000 hours average stressrupture life at 2125° F (1163° C) and 4000 psi (28 MN/m^2) in helium, but was microstructurally unstable at intermediate temperatures. A method of alloy design was demonstrated which was based on a linear relationship between the amount of Co₂W, the embrittling phase in this cobalt-tungsten alloy series, and the average electron vacancy concentration \overline{N}_{u} . Of several modifications of VM-103 the most favorable was VM-108, with a nominal composition in weight percent of 17.5 tungsten - 3 chromium - 5 nickel -5 iron - 0.37 zirconium - 0.75 titanium - 0.5 carbon - 3 rhenium and the balance cobalt. This alloy proved to be essentially microstructurally stable. After aging for 500 hours at 1400° F (760° C), the ultimate tensile strength and elongation measured at room temperature were unchanged from the as-cast alloy. Its average stress-rupture life at 2125° F (1163° C) and 4000 psi (28 MN/m²) in helium was over 2000 hours, similar to that of VM-103. Its incipient melting temperature was between 2475° and 2500° F (1357° and 1371° C), approximately 50° F (28° C) below that of VM-103, but about 100° F (56° C) higher than that of the highest melting point cast nickel-base alloys.

INTRODUCTION

Cobalt-base alloys are being used today for various high-temperature applications. The need for continually higher turbine inlet temperatures to meet the increased performance requirements of turboject engines and of the gas turbine powerplants of

advanced space power systems makes alloys based on cobalt appear attractive. This report deals with the development of a microstructurally stable high-strength cobalt-base alloy with potential for stator vane application in advanced gas turbines.

Although nickel-base alloys currently are the workhorse materials for the hot components of gas turbine engines, these materials drop off sharply in strength above 1900° to 2000° F (1038° to 1093° C). There are only a few exceptions to this, such as thoria-dispersion-strengthened nickel (ref. 1) and two very recently developed cast nickel-base alloys, NX-188 (ref. 2) and WAZ-20 (ref. 3), having high incipient melting temperatures (2375° F; 1302° C). This tendency toward a sharp decline in strength above 2000° F (1093° C) detracts from the usefulness of most nickel-base alloys as high-temperature engine components, such as the first-stage turbine stator vanes. One way of achieving higher strength materials for use at temperatures above 2000° F (1093° C) is to more fully exploit cobalt-base materials. Since cobalt has a higher melting point (2720° F; 1493° C) than nickel (2650°; 1454° C), it would seem likely that cobalt-base alloys could be designed with higher incipient melting temperatures and greater high-temperature strength than nickel-base alloys. Of course, for long-time service at 2000° F (1093° C) and above, under gas turbine operating conditions, suitable coatings must be provided for both nickel- and cobalt-base alloys.

Earlier work at NASA (refs. 4 and 5) with the cobalt-tungsten system established several new alloys with superior high-temperature strength for potential space power system applications. The significant differences between these alloys and existing cobalt-base alloys lay in their lower (zero to 3 percent) chromium content and higher tungsten content (25 percent). The lower chromium was intended to reduce the danger of material deterioration from evaporation in the high-vacuum space environment compared to that in conventional cobalt alloys, which contain between 19 and 25 percent chromium. The higher tungsten was intended to provide strengthening at high temperatures with a low vapor pressure element. Despite their low chromium content, these alloys did not oxidize catastrophically in air tests at high temperatures. One of the strongest alloys in this series, with a composition in weight percent of 25 tungsten (W) -3 chromium (Cr) - 1 titanium (Ti) - 1 zirconium (Zr) - 0.4 carbon (C) and the balance cobalt (Co), was chosen as the basis for a continuing investigation to achieve a potential stator vane material for advanced engines. Vacuum melting techniques were applied. The average electron vacancy concept was used in the design of a microstructurally stable alloy. Strength properties were obtained over a range of temperatures. Pertinent metallographic studies were made.

MATERIALS AND TEST PROCEDURE

Casting and Inspection Techniques

All test specimens were prepared by vacuum induction melting of virgin material. The forms and purities of the raw material were as follows:

Element	Form	Quoted purity, percent
Cobalt	Electrolytic	99. 9+ (Co+Ni)
Nickel	Electrolytic	99. 9+
Tungsten	Powder	99.9+
Chromium	Electrolytic	99.8+
Titanium	Sponge	99。3+
Zirconium	Sponge	99, 9+
Iron	Electrolytic	99.8+
Rhenium	Powder	99. 9+
Carbon	Graphite (granular)	98+

Induction melting was done in stabilized zironia (ZrO_2) crucibles. Before each melt was poured, the chamber was backfilled to 300 torr (40 000 N/m 2) of argon. Pour temperature, as determined by an optical pyrometer was 3100° F (1704 $^{\circ}$ C). Zircon shell molds imbedded in fire-clay grog and held at 1600° F (871 $^{\circ}$ C) by a resistance mold heater were used. Each casting consisted of a cluster of tensile test bars. After casting, the molds were allowed to remain in the vacuum chamber for 15 minutes. They were then removed and allowed to cool to room temperature (in about 6 hr) before knockout and cutoff. Before testing all specimens were vapor-blasted and inspected by radiographic and fluorescent penetrant techniques. Chemical analyses of selected heats of the most favorable alloy, VM-108, were made by wet chemical methods at an independent laboratory.

Specimens

The same type of specimen was used to determine as-cast stress-rupture and tensile properties. These specimens were cast to final dimensions and had conical shoulders with a 20° included angle. The gage section was 1. 20 inches (3.05 cm) long and 0.25 inch (0.635 cm) in diameter.

Tensile and Stress-Rupture Tests

All tensile data were obtained in air. Tests were conducted on a hydraulically operated universal testing machine in accordance with ASTM recommended practice. Stress-rupture tests were conducted in air, in vacuum, and in purified helium. The test conditions for the various alloys considered are summarized in tables I to III. The equipment and procedure for vacuum testing are described in reference 6. Helium tests were run on constant load machines having 10:1 or 20:1 ratio lever arms. The specimens were surrounded by nickel alloy muffles placed inside conventional Kanthal wound stress-rupture furnaces. The helium (nominal 99.9 percent purity) flow was directed through the muffles, thus providing an inert gas environment for the test specimen.

Metallographic Examination

Metallographic specimens were prepared by grinding through 600 grit abrasive paper and then mechanical polishing, finishing with 1/2 micrometer gamma alumina. The etchant used was 30 grams of lactic acid, 30 milliliters each of water and acetic acid, and 10 milliliters of hydrofluoric acid. Six drops of hydrogen peroxide were added to this mixture.

For quantitative measurements of precipitate particles the line intercept method was used. A grid containing four 3-inch (7.6 cm) lines drawn at random within a 4- by 5-in. (10.2- by 12.7-cm) frame was prepared. This grid was superimposed on photomicrographs having a magnification of 500. The number of intersections between the grid and platelets was counted and recorded. This value was assumed to be proportional to the volume fraction of the precipitate.

X-ray diffraction analyses were made to identify specific phases of interest. Samples for identification were residues obtained by electrolytic separation (extraction). X-ray diffraction patterns were made using a standard 114.6-millimeter Debye-Scherrer camera.

INVESTIGATIVE APPROACH

Base Alloy

The material selected as a base for this investigation was the NASA Co-25W-3Cr-1Ti-1Zr-0.4C alloy which is discussed in reference 5. Since this alloy was argon melted

we have designated it here as AR-103. For this investigation the alloy was vacuum melted and is designated VM-103. Its composition and that of cobalt alloys described in this report are shown in table IV along with their respective $\overline{N}_{_{Y\!Y}}$ values calculated by the method described in appendix A. The stress-rupture properties of VM-103 at 2000° and 2125° F (1093° and 1163° C) in helium are shown in figure 1. These data are listed in table II. At 2125° F (1163° C) and a stress of 4000 psi (28 MN/m²) the alloy had an average life of over 2000 hours, thus suggesting a potential for high-temperature applications, such as stator vanes in advanced gas turbine engines. A check of intermediate temperature stability, however, showed the alloy was prone to severe embrittlement between 1200° and 1600° F (649° and 871° C). This was reflected in a sharp drop in room-temperature ductility from 2 percent to an average of 1/2 percent together with a marked increase in tensile strength, as shown in figure 2. The individual tensile data points are listed in table I. The loss of ductility and increase in strength is associated with the Widmanstatten precipitate shown in figure 3. The precipitate was identified as Co₂W by X-ray diffraction analysis of residues electrolytically extracted with 25 percent phosphoric acid in water. Because the maximum strength and minimum ductility occur between 1400° and 1600° F (760° and 871° C) (fig. 2), it is assumed that the precipitation of Co₃W follows isothermal transformation kinetics of "C" curve type.

Effect of Iron and Nickel Additions

Since Drapier, de Brouwer, and Coutsouradis (ref. 7) had previously indicated that ${\rm Co_3W}$ forms in hexagonal areas of Co-W-Cr alloys, and since iron and nickel are known to stabilize the face-centered cubic phase in cobalt, additions of iron and nickel were made to the alloy to reduce the tendency to form the hexagonal phase. The results of these additions on alloy stability are shown in figure 4. It can be seen that nickel additions were more effective than iron in reducing the amount of ${\rm Co_3W}$ formed. However, neither addition totally eliminated the instability. Marked reductions in the $1850^{\rm O}$ F ($1010^{\rm O}$ C), 15 000 psi ($104~{\rm MN/m}^2$) stress-rupture life occurred with increasing nickel and iron content. Because the life-stability tradeoffs from this procedure were not acceptable, another alloying approach was sought to achieve suitable high-temperature strength together with stability.

Use of Electron Vacancy Concentration Concept

References 8 and 9 have shown that it is possible to predict with reasonable accuracy whether or not an alloy will form sigma phase by calculating the average electron-

vacancy concentration \overline{N}_V of the residual matrix after other phases such as gamma prime or carbides have formed. If the calculated average electron vacancy number is below the cutoff point for stability as determined from experimental data for representative nickel-base alloys, sigma phase would not be expected to form.

We thought it reasonable to look for similar behavior with respect to Co_2W in this alloy system and hypothesized that the amount of Co₃W formed was linearly related to \overline{N}_{u} . Thus, a procedure similar to that of reference 8 and which is described in detail in appendix A, was used to calculate the \overline{N}_v values of various alloys in this alloy system. The compositions were deliberately varied by varying the elements over the ranges shown in table V to give a range of \overline{N}_{v} . These compositions were melted and exposed at the chosen screening condition (192 hr at 1600° F (871° C)). This condition was believed to be above the nose of the time-temperature-transformation curve for formation of this phase. Using a condition above the nose of the curve would show trends more easily than using a condition at the nose. By metallographic examination in the manner described previously, the amount of Co3W precipitate formed in each alloy was determined. The amount of Co₃W formed in each alloy was plotted against N_v (fig. 5) for two constant levels of iron content, zero and 5 percent. The data were treated in this way with regard to iron content because iron has two opposite effects on Co₃W formation. As previously indicated, it stabilizes the cubic phase in this system, yet increases \overline{N}_{v} . Since iron has a higher N_v than cobalt, iron additions raise the N_v of the alloy. A straight line determined by the method of least squares was drawn through the zero iron data. The statistical significance of this line was 95 percent. The equation of this line, which gives the amount of Co₂W, is

$$Co_3W = 2255 \overline{N}_V - 4296$$
 (1)

Comparison of equation (1) with equation (B1) (appendix B), which describes the amount of Co_3W formed in the binary Co-W system at 1600^{O} F (871°C), shows a striking similarity The $\overline{\text{N}}_{\text{V}}$ intercept for zero Co_3W content from equation (1) is 1.91 compared to 2.00 predicted from the binary phase diagram. The behavior shown by this analysis of the binary system (appendix B) supported our hypothesis that the amount of Co_3W formed in a complex alloy during isothermal exposure could be approximated by a linear function of $\overline{\text{N}}_{\text{V}}$.

By extrapolating to a zero Co_3W content, the critical $\overline{\text{N}}_v$ for Co_3W could be obtained. To be conservative (for alloy development) in determining the criticl $\overline{\text{N}}_v$ for 192-hour exposure at 1600° F (871°C), lines connecting the points along the lower limit of the ranges of experimental data for the zero iron and 5 percent iron content were extrapolated to zero Co_3W content. These may be seen from figure 5 to give critical $\overline{\text{N}}_v$ values of 1.87 for zero iron and 2.04 for 5-percent-iron-content alloys.

RESULTS AND DISCUSSION

Evaluation of Alloy Design Technique

Alloy VM-106 was formulated on the basis just described to be stable for 192 hours at 1600° F (871°C). Its composition, shown in table IV, has an \overline{N}_v of 2.03. Figure 6 shows a photomicrograph of VM-106 after it was exposed to 1600° F (871° C) for 192 hours. There is no evidence of Widmanstätten precipitate, suggesting the alloy is stable. To verify stability of mechanical properties, the room-temperature tensile properties of the alloy were determined after various exposures. The results are listed in table III along with the as-cast data. Compared to the as-cast data, there was only a slight change in ductility after exposure at 1600° F (871° C) for 192 hours and at 1642° F (894°C) for 1000 hours. But there was a loss of ductility after 500 hours exposure at 1435° F (779° C). The latter was anticipated because the precipitation of Co₃W was believed to follow TTT curve kinetics with a maximum rate of precipitate probably occurring between 1400° and 1600° F (760° and 871° C). Photomicrographs of the alloy VM-106 after exposure at various temperatures are shown in figure 7. It can be seen that the alloy forms a Widmanstätten precipitate near 1400° F (760° C) and a general darkening of the structure occurs near 1200° F (649° C). The source of the latter is unknown; however, its effect on mechanical properties does not appear important. Both the metallographic evidence and the results of the tensile tests made after allov VM-106 was exposed 192 hours at 1600° F (871° C) however, verify the usefulness of the design technique. Thus, alloy VM-106 was essentially stable for the condition of time and temperature for which the correlation between \overline{N}_v and amount of Co_3W was determined.

The same technique could have been applied to establish a critical \overline{N}_V for stability after exposure at 1400° F (760° C). This would, however, have involved quantitative metallographic measurements of the amount of Co_3W formed after such exposure in all of the alloys used to obtain a correlation of \overline{N}_V with Co_3W such as that shown in figure 5. Extrapolation to a \overline{N}_V value corresponding to zero Co_3W would then have indicated what a stable composition would be. Since we had already obtained an indication of the direction to go with respect to compositional changes to achieve stability and had an intuitive grasp of the alloy system, it was considered most expeditious simply to increase the nickel content of VM-106. As a result of an additional nickel modification, alloy VM-108 (table IV) was formulated. Physical and mechanical properties and stability determinations for this alloy are discussed in the next section.

Properties of Alloy VM-108

Chemical analyses of randomly selected heats of alloy VM-108 are shown in table VI.

These all come very close to the desired nominal composition shown in table IV. Also listed in table VI are the \overline{N}_v values for these heats calculated as described in appendix A. It should be noted that in all cases the \overline{N}_v was equal to or less than 2.0.

Tensile properties. - The variation of tensile strength and elongation with temperature is shown in figure 8, and individual values are listed in table I. The strength varies from approximately 87 000 psi (600 MN/m²) at room temperature to 16 000 psi (110 MN/m²) at 2100° F (1149° C). The average elongation increases from $2\frac{1}{2}$ percent at room temperature to 27 percent at 2100° F (1149° C). These values are reasonably close to those obtained with the basic NASA alloy AR-103 (ref. 5), which varied from approximately 96 000 psi (662 MN/m²) at room temperature to 20 000 psi (138 MN/m²) at 2100° F (1149° C). The elongation of the AR-103 alloy was $2\frac{1}{2}$ percent at room temperature and 35 percent at 2100° F (1149° C).

Stress-rupture properties. - The variation of time-to-rupture of alloy VM-108 with stress at $2000^{\rm O}$ and $2125^{\rm O}$ F ($1093^{\rm O}$ and $1163^{\rm O}$ C) is shown in figure 9, and individual values are listed in table II. At $2125^{\rm O}$ F ($1163^{\rm O}$ C) the average rupture life varied from approximately 50 hours at 8000 psi (55 MN/m^2) to 2100 hours at 4000 psi (28 MN/m^2). This compares well with alloy VM-103, which varied from approximately 135 to 2250 hours under similar conditions (fig. 1). No consistent effect on life was observed as a result of testing in vacuum and helium atmospheres. After testing some specimens were bright and others were darkened. The darkening was believed to be due to oxidation for the specimens tested in vacuum and brightening due to carburization from sealing oil vapor for those tested in helium. The rupture ductilities, although not always obtainable, were generally of the order of 15 to 20 percent.

<u>Physical properties</u>. - The densities of alloys VM-103 and VM-108 were determined by weighing samples in and out of water. Alloy VM-108 has a density of 9.7 grams per cubic centimeter and VM-103 has a density of 10.1 grams per cubic centimeter.

The incipient melting point was determined by exposing samples cut from cast bars for 2 hours at various temperatures in a heat-treating furnace. Subsequent examination indicated that incipient melting in VM-108 occurred at 2500° F (1371° C) and not at 2475° F (1357° C). This is approximately 50° F (28° C) below the incipient melting temperature of VM-103 but 100° F (56° C) higher than that of the highest melting point cast nickel-base alloys.

Stability. - To check stability, the alloy was aged at 1400° F (760° C) for 500 hours, then tensile tested at room temperature. The average tensile strength of two tests was 98 700 psi (681 MN/m^2), and the elongation was 3 percent. These values are essentially unchanged from the as-cast condition (fig. 8). Metallographic examination of the alloy after this exposure showed only a trace of a Widmanstätten precipitate. This is shown in figure 10.

SUMMARY OF RESULTS

The previously developed NASA cobalt-tungsten (Co-W) alloy series was investigated with a view toward achieving a high-temperature cobalt-base alloy with potential for stator vane application in advanced gas turbine engines. The following major results were obtained:

- 1. A vacuum-melted modification of the cobalt (Co) 25 tungsten (W) 3 chromium (Cr) 1 titanium (Ti) 1 zirconium (Zr) 0.4 carbon (C) alloy (herein designated VM-103) had an average stress-rupture life at 2125° F (1163° C) and 4000 psi (28 MN/m²) in helium of more than 2000 hours. However, upon exposure at intermediate temperatures of 1200° to 1600° F (649° to 871° C), the Co₃W phase formed in a Widmanstatten morphology and drastically reduced the ductility of the alloy.
- 2. By varying the amounts of the elements in VM-103 and introducing iron (Fe), nickel (Ni), and rhenium (Re), compositions of different \overline{N}_v were obtained. The amount of Co_3W formed in the resulting alloys after 192 hours exposure at 1600^{O} F (871°C) could be approximated by a linear function of \overline{N}_v for a constant Fe content. Extrapolation to a zero Co_3W content gave a critical value of \overline{N}_v below which this alloy system should be stable. This technique was verified with alloy VM-106.
- 3. Of several modifications of alloy VM-103, VM-108 was the most favorable. It had a nominal composition in weight percent of 17.5 W-3 Cr-5 Ni-5 Fe-0.37 Zr-0.75 Ti-0.5 C-3 Re and the balance Co. The alloy was essentially microstructurally stable. After aging for 500 hours at 1400° F (760° C) the ultimate tensile strength and elongation measured at room temperature were unchanged from the as-cast alloy. Its average stress-rupture life at 2125° F (1163° C) and 4000 psi (28 MN/m 2) in helium was also over 2000 hours, similar to that of VM-103. Its incipient melting temperature was between 2475° and 2500° F (1357° and 1371° C), approximately 50° F (28° C) below that of VM-103, but about 100° F (56° C) higher than that of the highest melting point cast nickel-base alloys.

Lewis Research Center,

National Aeronautics and Space Administration, Cleveland, Ohio, October 30, 1970, 129-03.

APPENDIX A

CALCULATION OF AVERAGE ELECTRON VACANCY NUMBER

The calculation of average electron vacancy number (\overline{N}_V) followed the procedure proposed by Woodyatt, Sims, and Beattie (ref. 8). Briefly, the procedure is as follows: various assumptions must be made as to the manner in which the elements present in the alloy are partitioned in forming carbides, borides, or gamma prime. The amounts of the various elements remaining after such phase formation, scaled to 100, are equivalent to the residual matrix composition. Electron vacancy numbers are assigned to each element. The average electron vacancy number of the residual matrix is then determined by summing up the products of the atomic fraction of each element times its electron vacancy number.

Since the technique was developed primarily for gamma prime strengthened alloys, the only portion of their system used was their carbon partitioning scheme and the final calculation steps for $\overline{N}_{\rm v}$.

Their assumption that one-half of the carbon forms monocarbides (MC) and the remainder forms complex carbides did not agree with X-ray diffraction data obtained from extracted residues in this alloy system. Specifically, no complex carbides were found in the cobalt alloy when it was aged to cause Co_3W precipitation. It was observed that our assumption that all the carbon present initially would form simple MC carbides (until M is depleted) and would then form complex carbides also did not agree with the X-ray data.

Electron microprobe analyses of several carbide particles showed that different assumptions regarding the MC carbides were required. These analyses are summarized in table VII. Of particular importance is the fact that both tungsten and cobalt have high solubility in the titanium and zirconium carbides. This information was then incorporated into the calculation by assuming that the titanium and zirconium carbides are $(Ti, Zr)_{0.6} W_{0.25} Co_{0.15} C$.

A model which assumes this ''alloy'' monocarbide forms prior to a complex carbide (carbon goes preferentially to the monocarbide) would predict that no complex carbides would be found in most of the compositions examined. In those few compositions where it would be anticipated, only a small amount of carbon would be available, and it is quite conceivable that M_6 C was not observed by X-ray diffraction because the quantity of the predicted complex carbide was below detection limits.

The calculation procedure to determine $\stackrel{-}{N}_{V}$ used in this report consisted of the following steps:

- (1) Convert weight to atomic percent
- (2) Deplete matrix assuming $(Zr_{0.6} W_{0.25} Co_{0.15}) C$ forms

- (3) Deplete matrix assuming $(\mathrm{Ti}_{0.6}\mathrm{W}_{0.25}\mathrm{Co}_{0.15})$ C forms
- (4) Deplete matrix assuming remaining carbon forms M₆C of form Co₃ (Cr + W)₃ C
- (5) Calculate \overline{N}_v as follows:

$$\overline{N}_{\mathbf{v}} = \sum_{n=1}^{n} \mathbf{F}_{n} \mathbf{N}_{\mathbf{v}_{n}}$$

where $\mathbf{F}_{\mathbf{n}}$ is the atomic fraction of the \mathbf{n} element and

$$N_{v, Ni} = 0.61$$
 (from ref. 9)
 $N_{v, Co} = 1.71$ (from ref. 8)
 $N_{v, Fe} = 2.66$ (from ref. 8)
 $N_{v, Re} = 3.66$
 $N_{v, W} = N_{v, Cr} = 4.66$

 $N_{v. Ti} = N_{v. Zr} = 6.66$

The relation, 10.66 minus the group number, was used to obtain the $\,\rm N_{_{V}}\,$ values for Cr, Re, W, Zr, and Ti.

APPENDIX B

Relation between $\overline{\mathrm{N}}_{\mathrm{v}}$ and amount of $\mathrm{Co}_{3}\mathrm{W}$ in binary co-w system

If one considers the average electron vacancy concentration as a substitute for atom concentration in constructing a phase diagram, a schematic representation such as that shown in figure 11 results. In this figure, the single-phase region represents the face-centered cubic cobalt terminal solid solution. $A_x B_y$ represents the $\text{Co}_3 W$ intermetallic compound. For a given temperature an isotherm would intersect the solvus at the equilibrium concentration or $\overline{N}_{v.\, \text{critical}}$.

According to the Lever rule, the relative amount of a phase in a two-phase region of a binary phase diagram is a linear function of the concentration of either alloying element. As shown in appendix A, $\overline{\rm N}_{\rm V}$ is a linear function of concentration. In terms of the diagram (fig. 11) the relative amount of a phase is then also a linear function of $\overline{\rm N}_{\rm V}$. Thus, the equilibrium percentage of ${\rm Co_3W}$ formed at $1600^{\rm O}$ F (871 $^{\rm O}$ C) is

$$Co_3W = 227 \overline{N}_V \sim 454$$
 (B1)

in the binary cobalt-tungsten system. The \overline{N}_v can be calculated using the N_v values of cobalt and tungsten from appendix A. The \overline{N}_v of Co_3W is 2.44. The solubility limit of the terminal Co-W solid solution is 10 atom percent at 1600^{O} F (871°C) according to reference 10. This is equivalent to an \overline{N}_v critical of 2.00.

REFERENCES

- 1. Wolf, J., ed.: Aerospace Structural Metals Handbook. Vol. II-A. Non-Ferrous Alloys. Belfour Stulen, Inc. (AFML-TR-68-115), 1970.
- 2. Maxwell, D. H.: The Development of an Advanced Turbine Vane Alloy. Rep. GP-69-186, Pratt & Whitney Aircraft, June 2, 1969.
- 3. Waters, William J.; and Freche, John C.: A Nickel-Base Alloy, WAZ-20, with Improved Strength in the 2000° to 2200° F Range. NASA TN D-5352, 1969.
- 4. Freche, John C.; Ashbrook, Richard L.; and Klima, Stanley J.: Cobalt-Base Alloys for Space-Power Systems. J. Metals, vol. 15, no. 12, Dec. 1963, pp. 928-934.
- Freche, J. C.; Ashbrook, R. L.; and Sandrock, G. D.: High-Temperature, Cobalt-Tungsten Alloys for Aerospace Applications. J. Eng. Industry, vol. 87, no. 1, Feb. 1965, pp. 9-20.
- 6. Buzzard, Robert J.: High Temperature Creep-Rupture Properties of a Tungsten-Uranium Dioxide Cermet Produced from Coated Particles. NASA TM X-1625, 1968.
- 7. Drapier, J. M.; de Brouwer, J. L.; and Coutsouradis, D.: Refractory Metals and Intermetallic Precipitates in Cobalt-Chromium Alloys. Cobalt, no. 27, June 1965, pp. 59-72.
- 8. Woodyatt, L. R.; Sims, C. T.; and Beattie, H. J., Jr.: Prediction of Sigma-Type Phase Occurrence from Compositions in Austenitic Superalloys. Trans. AIME, vol. 236, no. 4, Apr. 1966, pp. 519-527.
- 9. Boesch, William J.; and Slaney, John S.: Preventing Sigma Phase Embrittlement in Nickel Base Superalloys. Metal Prog., vol. 86, no. 1, July 1964, pp. 109-111.
- 10. Hansen, Max; and Anderko, Kurt: Constitution of Binary Alloys. Second ed., McGraw-Hill Book Co., Inc., 1958.

TABLE I. - TENSILE DATA FOR ALLOYS VM-103 AND VM-108

	Test ter	mperature	Ultimate tens	ile strength	Elongation
	OF	°С	psi	MN/m ²	percent
		VM	-103		•
As cast	Room	Room	97 700	674	2
After 192 hr					
exposure at					ļ
following					
temperatures,					
1200° F (649° C)]]		118 700	819	1
			114 100	787	1
1400 ⁰ F (760 ⁰ C)			141 500	976	0
			141 900	979	1
1600° F (871° C)			140 500	970	1
	ļ		134 500	928	0
1800 ^o F (982 ^o C)			88 300	609	2
			89 400	617	2
2000 ^o F (1093 ^o C)			89 600	618	3
		*	90 300	623	3
		VM-	108		
As cast	Room	Room	89 800	620	3
	Room	Room	87 500	604	2
	1200	649	60 300	416	5
	1500	816	57 400	396	5
	1650	899	41 900	289	11
	1650	899	43 100	297	10
	1800	982	34 300	237	24
	1950	1066	21 100	146	28
	1950	1066	20 900	144	47
	2100	1149	15 100	104	27
After 500 hr at	į.	Room	102 100	705	2
1400° F (760° C)	Room	Room	95 300	658	4

TABLE II. - STRESS-RUPTURE DATA FOR ALLOYS VM-103 AND VM-108

	(a) VM-103							(b) VN	1-10 8		
Test en-	}	rature	Str	ess	Time	Test en-		erature	Str	ess	Time,
vironment	o _F	°C	psi	MN/m ²	hr	vironment	$^{ m o}_{ m F}$	°C	psi	MN/m ²	hr
Helium	2000	1093	20 000	138	0.5	Air	1850	1010	15 000	104	32.7
					.6						33.1
			15 000	104	3.5						62.6 39.3
					2.4	<u></u>					39.3
					3.7	Helium	2000	1093	12 000	83	23.3
					88.7						8.0
			10 000	69	243.0				10 000	69	240.6
					136.3						131.4
		ļ			92.4						148.6
	2125	1163	10 000	69	8.0						146.2
					2.6				_		182.2
					19.6				8 000	55	416.4
			8 000	55	a _{212.0}						398.9
			0 000	33	151.6						65.2
					191.7	Vacuum	2000	1093	8 000	55	585.3
					105.3	i					
					99.0	Helium	2125	1163	8 000	55	38.2
	ļ				83.8	:					94.2
					91.8						31. 2 37. 3
			6 000	41	116.8						37.3
											69.3
			4 000	28	a3460.0	T/2 2	0105	1100	0.000		40.0
					1300.3 1977.0	Vacuum	2125	1163	8 000	55	40.8
					1011.0	Helium	2125	1163	7 000	48	187.9
											80.3
						Vacuum	2125	1163	6 000	41	481.3
					1						414.1
						Helium	2125	1163	6 000	41	643.7
						Vacuum	2125	1163	4 000	28	1497.0
a _m	l :	l i	l	l	ļ	ŀ		ļ	J		2682.0

^aTest stopped before specimen failed.

TABLE III. - TENSILE PROPERTIES OF VM-106

AT ROOM TEMPERATURE

Condition	Ultimate tens	sile strength	Elongation,
	psi	MN/m ²	percent
As-cast	90 330	623	3
	92 680	640	3
Exposed 1000 hr at 1230° F (666° C)	126 900	876	3
Exposed 500 hr at 1435° F (779° C)	100 500	693	1
Exposed 1000 hr at 1640° F (893° C)	81 300	561	2
Exposed 192 hr	87 800	605	2
at 1600° F (871° C)	88 700	612	2

TABLE IV. - NOMINAL COMPOSITIONS OF NASA

COBALT-BASE ALLOYS INVESTIGATED

Alloy		Composition, wt. %									
	w	Cr	Ni	Fe	Zr	Ti	C	Re	Co	electron	
			l					l		vacancy	
1										concentra-	
ĺ		ľ		1			ĺ			tion,	
			İ							\overline{N}_v	
]]]	l			(a)	
AR-103	25	3	-	-	1	1	0.4	-	Bal.	2.11	
VM-103	25	3	-	-	. 5	1	. 4	-	Bal.	2, 11	
VM-106	17.5	3	1	5	. 37	. 75	. 5	3	Bal.	2.03	
VM-108	17.5	3	5	5	. 37	. 75	. 5	3	Bal.	1,98	

^aCalculated by method described in appendix A.

TABLE V. - ELEMENTS VARIED IN AVERAGE ELECTRON VACANCY CONCENTRATION EXPERIMENT AND THEIR COMPOSITIONAL RANGE

Element	Range, wt. %					
	Minimum	Maximum				
Ni	0	10				
w	17.5	25				
Ti	. 75	1.0				
Zr	. 37	. 5				
С	. 4	. 6				
Re	0	3				
Fe	0	10				

TABLE VI. - CHEMICAL ANALYSIS OF RANDOM HEATS

OF ALLOY VM-108

	Composition, wt. %									
w	Ni	Fe	Cr	Re	Ti	Zr	С	Co	electron	
									vacancy	
									concentra-	
									tion,	
									\bar{N}_v	
									(a)	
17.10	5.30	5.12	3.01	2.96	0.78	0.37	0.49	Bal.	1.98	
17.18	5.31	5.06	2.95	3.00	. 80	. 38	. 45	Bal.	2.00	
17.23	5.28	5.07	3.04	3.02	. 76	. 38	. 45	Bal.	2.00	

^aCalculated by method described in appendix A.

TABLE VII. - RANGE OF MICROPROBE ANALYSES $\qquad \qquad \text{OF MONOCARBIDES } (\text{MC})^{\text{a}}$

Carbide	rbide "'M" portion element, at.%								
type	Ti	Zr	Co	w	Cr				
Ti	44 to 60	4 to 10	8 to 30	18 to 27	0.7 to 2				
Zr	12 to 15	39 to 62	8 to 35	11 to 16	0. 4 to 4				

^aDetermination made from 14 particles for TiC and 5 particles for ZrC.

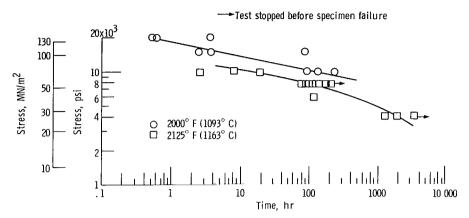


Figure 1. - Stress-rupture life of alloy VM-103 in helium.

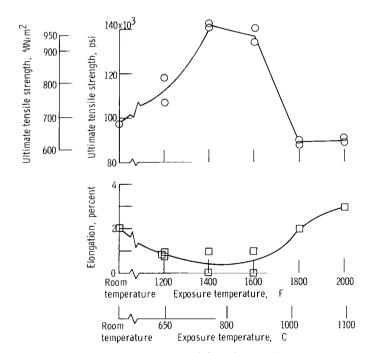


Figure 2. - Effect of elevated-temperature exposure on tensile properties of VM-103. Tests conducted at room temperature after 192 hours at temperature.



Figure 3. - Alloy VM-103 after 192 hours at 1600° F (871° C). (Original magnification, 1000).

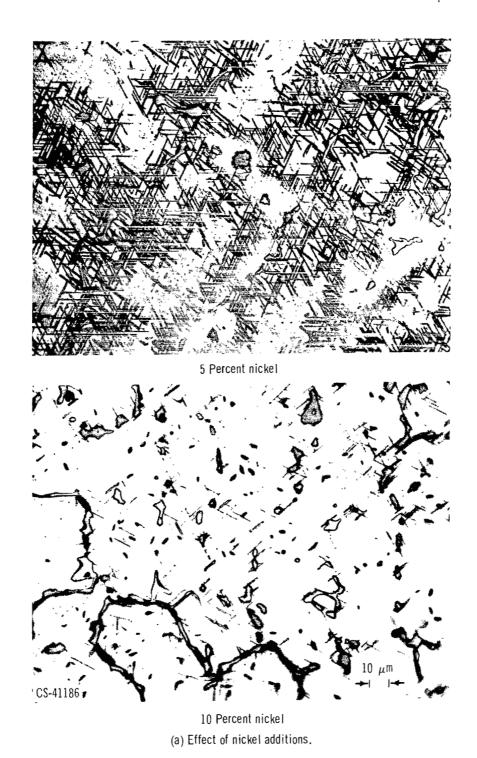
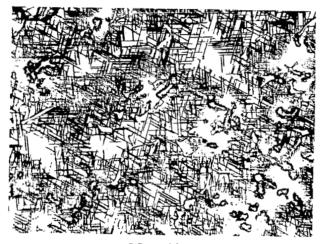


Figure 4. - Effect of alloying additions on microstructure of alloy VM-103 after 192 hours at 1600° F (871° C). (Original magnification, 500).

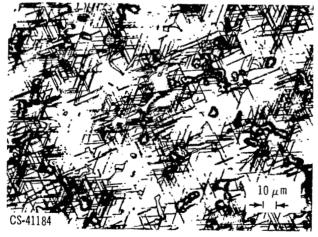




3 Percent iron



7 Percent iron



10 Percent iron

(b) Effect of iron additions.

Figure 4. - Concluded.

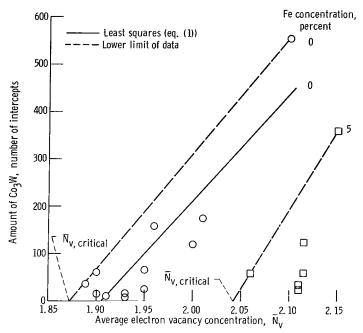


Figure 5. - Correlation between average electron vacancy concentration and amount of ${\rm CO_2W}$ in CO-W alloys. Exposure, 192 hours at 1600° F (871° C).

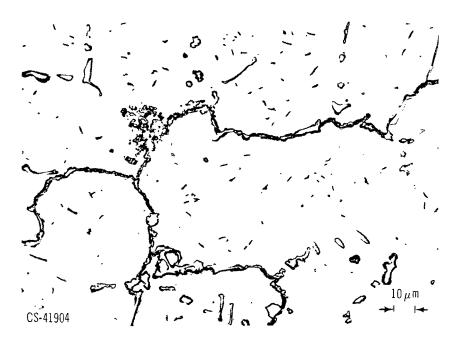
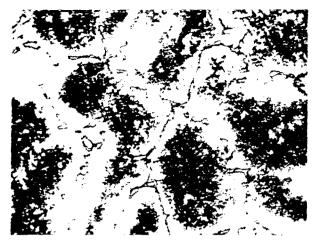
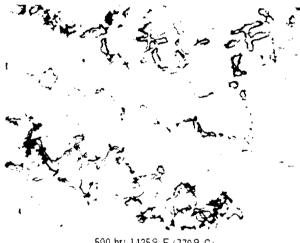


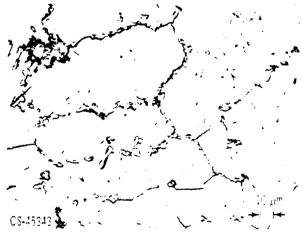
Figure 6. - Microstructure of alloy VM-106 after 192 hours at 1600° F (871° C). (Original magnification, 500).



1000 hr; 1230° F (666° C).



500 hr; 1435° F (779° C).



1000 hr; 1640° F (893° C

Figure 7. - Effect of long time exposure at elevated temperatures on NASA cobalt alloy VM-Lio. (Original magnification, 500).

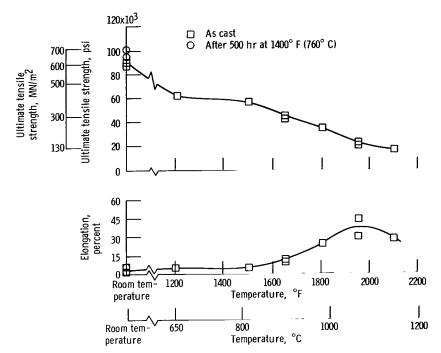


Figure 8. - Effect of temperature on tensile properties of VM-108.

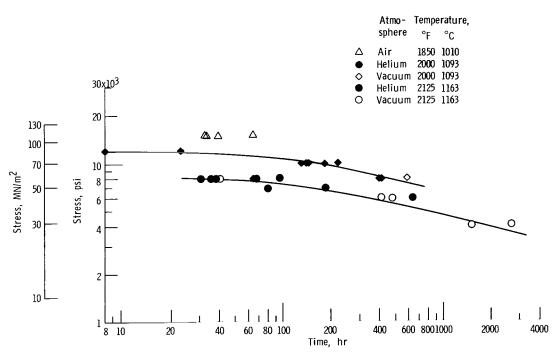


Figure 9. - Stress-rupture life of VM-108.

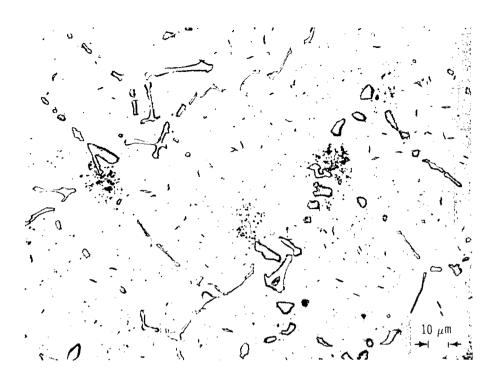


Figure 10. - Effect of 500 hours exposure at 1400 $^\circ$ F (760 $^\circ$ C) on microstructure of VM-108 alloy. (Original magnification, 500).

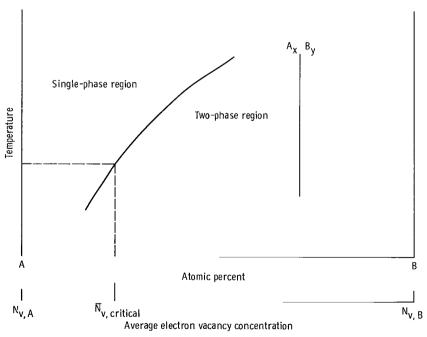


Figure 11. - Schematic phase diagram in terms of atomic percent and electron vacancy concentration.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, D. C. 20546

OFFICIAL BUSINESS

FIRST CLASS MAIL



POSTAGE AND FEES PAID NATIONAL AERONAUTICS AN SPACE ADMINISTRATION

CIU OCI 42 51 3US 71028 00903 AIR FORCE VEAPONS LABURATORY /WLOL/ KIRTLAND AFB, NEW MEXICO 87117

ATT E. LOU SOWMAN, CHIEF, TECH. LIBRARY

POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

"The aeronantical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS:

Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION

PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546